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(71) Applicant (*for all designated States except US*): ERTE-
CEE B.V. [NL/NL]; Textielstraat 30, NL-7575 CA Olden-
zaal (NL).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): NOORDEGRAAF,
Jan [NL/NL]; Blauwe Hof 41-01, NL-6602 ZX Wijchen
(NL). RENSEN, Petrus, Frederikus, Maria [NL/NL];
Rijnstraat 41, NL-6686 MH Doornenburg (NL). BUIJK,
Christianus, Marcus, Gijsbertus, Maria [NL/NL]; Hab-
sburglaan 71, NL-5616 HE Eindhoven (NL). KEMPER-
MAN, Wilhelmus, Petrus, Theodorus [NL/NL]; De Kuil
40, NL-5527 AA Hapert (NL). DE SWART, Henricus, Jo-
hanna [NL/NL]; Gaarde 83, NL-5103 EB Dongen (NL).

(74) Agents: DOHMEN, Johannes, Maria, Gerardus et
al.; Algemeen Octrooi- en Merkenbureau, P.O. Box 645,
NL-5600 AP Eindhoven (NL).

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(54) Title: METHOD FOR MANUFACTURING A FIRE RETARDANT COMPOSITE AND COMPOSITE THUS OBTAINED

(57) Abstract: The present invention relates to a method of manufacturing a fire retardant composite, a composite of a foamed polymer having a coating with fire retardant properties, and also the use of such composites. The method according to the present invention comprises the following steps: i) providing beads of foamed polymer, ii) applying a coating on the beads of step i) and iii) shaping the thus coated beads into said composite.

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Method for manufacturing a fire retardant composite and composite thus obtained.

The present invention relates to a method of manufacturing a fire retardant composite, a composite of a foamed polymer having a coating with fire retardant properties, and also the use of such composites.

US 5 462 699 relates to a fire retardant composition for application to, *inter alia*, building materials, the composition containing a silicate, water and surfactant.

Other routes for manufacturing a fire retardant coating to be applied on a foamed polymer are e.g.:

sodium silicate + esters (e.g. diacetin or triacetin),
sodium silicate + aluminum tripolyphosphate,
sodium silicate + calcium phosphate,
sodium silicate + aluminum sulphate.

The problem with using a silicate based fire retardant composition for building insulation materials such as expanded polystyrene (e.g. roofing insulation) is that, until needed, such materials are often left exposed to the adverse weather conditions after delivery to the building site. Unless precautions are taken to protect them against the wet, such exposure can result in significant loss of the mechanical and fire retardancy properties of the silicate-based composition.

Soluble silicates are widely used as adhesives, coatings and bondings. Whilst their inherent solubility is an asset in many of the applications for which they are used, it is disadvantageous for applications where, for example, water resistance, integrity and strength of structure are deemed essential.

Considerable efforts have been made to minimise the solubility of silicates in compositions of the kind referred to above,

for example by addition of metal (such as calcium and magnesium) salts. However, addition of such salts tends to result in a precipitated form rather than a product with a continuous networklike structure. The soluble salt formed in the precipitation reaction is deleterious to the physical integrity of the applied film and hence ultimately, strength of the resultant product.

Factors such as these are a deterrent to the use of silicates in for example the production of fire retardant coating composition. Fire retardant coating compositions find wide application in the construction and building maintenance industries, for example for application to flammable building materials before, or after, their incorporation in a building structure. Examples of flammable materials are polymer tiling and sheeting, e.g. of expanded polystyrene or urethane plastics and composites containing such plastics. Wood, wood chip and paper based materials can also benefit from application of such coatings. Included within the class of fire retardant coating compositions are so-called intumescent coatings which exert their protectant action partly by swelling when exposed to heat or fire.

In some cases, flammable materials are sold with the fire retardant coating pre-applied. For example, an intumescent fire retardant coating known as SafeCoat E84TM is pre-applied to expanded polystyrene/polyurethane foam articles prior to sale.

We have now found that improved composites having an aqueous coating can be produced from silicates in such a way that the solubility problem discussed above is significantly counteracted thus making compositions according to the present invention suitable for use as fire retardant compositions.

Thus a first aspect of the present invention provides a method of manufacturing a fire retardant composite, the method comprising the following steps:

- i) providing beads of foamed polymer,

- ii) applying a coating on the beads of step i) and
- iii) shaping the thus coated beads into said composite.

According to a preferred embodiment of the present method step iii) is carried out in a press. Typically step iii) is carried out as a casting method. In another embodiment step ii) is carried out in a fluid bed, wherein the coating is sprayed onto the beads and an air flow is blown through the bed of beads. It is further preferred to carry out step ii) in an agitated bed, wherein the coating is sprayed on the beads, or to carry out step ii) in a mixer, for example a ribbon blender, wherein the coating is sprayed on the beads. It is furthermore possible to replace step iii) by steps iv), v) and vi), in which step iv) transferring the coated beads to a press, v) applying steam to the coated beads present in said press, and vi) releasing the composite from the press.

The foamed polymer is selected from PUR, PET, EPP, EPE, expanded polyvinyl arylenes or a combination thereof. Its density lies preferably within the range of 5 - 500 kg/m³, whereas the density of the foamed polymer plus the coating lies within the range of 10-1000 kg/m³, on a dried coating basis.

Another aspect of the present invention provides a method of manufacturing a fire retardant composite in which a coating is used, i.e. an aqueous gel-forming composition comprising an aluminosilicate and, if appropriate, an organic liquid which enhances the integrity of films formed by application of the composition as a coating to a surface of a foamed polymer followed by drying.

As used herein, the term "gel" refers to a substance that contains a continuous solid skeleton (in the present case based on the aluminosilicate) enclosing a continuous liquid phase (in the present case, predominantly water) - see for example Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing (C. J. Brinker and G. W. Scheer) published by Academic Press Inc.

In the absence of said organic liquid, we have found that the more extensive the drying, the more prone a film coating produced using the aluminosilicate composition is to result in a weak and powdery coating in a relatively short time. When the organic liquid is present
5 however, the integrity of the coating in terms of its strength and non-powdery nature is considerably improved.

The organic liquid is preferably one which is substantially water-immiscible. Usually the degree of immiscibility is such that, at 25 °C, the organic liquid dissolves to the extent of less than about 10%
10 by weight (preferably less than about 5 wt%) in water, or water dissolves to the extent of less than about 10 wt% (preferably less than about 5% by weight) in the organic liquid.

The aluminosilicate as used in the present invention is typically formed by the sol-gel route and this can be effected *in situ* by
15 forming the aluminosilicate at the point of use, by mixing precursor liquids. The present invention is limited to methods of manufacturing fire retardant composites, comprising beads of foamed polymer having a coating, the composites comprising beads of foamed polymer and their use as a construction material and an insulant. The present invention does
20 not extend to compositions comprising aluminosilicate, methods of making such compositions and precursor systems therefor and application systems for those precursor systems. However, a precursor system for forming a coating composition for application on foamed polymers in a method according to the first aspect of the invention may comprise:

- 25 (i) water and a metal aluminate;
(ii) water and a metal silicate; and, if appropriate,
(iii) said organic liquid.

A sol-gel is basically a reaction product which is initially formed as a liquid but which subsequently forms a gel and
30 ultimately solidifies.

At least part of the organic liquid may be incorporated in

component (i) and/or component (ii). Alternatively, it may initially be entirely separate from both of components (i) and (ii).

An application system for forming a coating composition from a precursor system as described above and applying the coating composition so formed to a foamed polymer substrate may comprise means for admixture of components (i), (ii) and (iii) and application means for effecting coating of the substrate with the resulting mixture.

Another aspect of the present invention provides a composite of foamed polymer having a coating with fire retardant properties wherein the coating is produced using an aqueous gel-forming composition, comprising an aluminosilicate composition, and one or more optional other ingredients.

The aqueous gel forming composition preferably comprises a film-integrity enhancing organic liquid. Typically the aluminosilicate composition is from 45% to 90% by weight, on basis of the dried coating, in which the aluminosilicate composition is from 50% to 85%, by weight, on basis of the dried coating. The moisture content of the dried coating is no greater than 40%, preferably no greater than 30% and more preferably no greater than 20% by weight, especially 16%, by weight. The coating further comprises at least one metal or metal oxide in an amount of up to 16%, preferably up to 8% by weight of the dried coating, in which the organic liquid comprises up to 16% by weight of the dried coating. Typically the aluminosilicate has a Si:Al mole ratio of from 3 to 30, typically up to 15, preferably up to 10.

The coating composition for application on the foamed polymer may comprise admixture of the following components:

- (i) water and a metal aluminate;
- (ii) water and a metal silicate; and, if appropriate,
- (iii) said organic liquid.

A further aspect of the present invention provides the use of a composite according to the present invention as a construction

material, especially in buildings, as well as an insulant, especially in buildings. The construction element is chosen from the group panel, door, sheeting, ceiling and tile. Another application of the present composite is as a construction material for packaging.

5 Coatings formed from compositions such as described above exhibit superior physical integrity and long term stability, in comparison with conventional silicate systems, by virtue of the aluminosilicate being present in the form of a network of bonded molecules that extends throughout the solution and by virtue of the
10 presence of said organic liquid.

Typically the composition prior to application to a foamed polymer comprises at least 5% by weight of the aluminosilicate, and 0 to 10% by weight of said organic liquid.

A preferred class of compositions to be used as a coating
15 on foamed polymers in a method according to the present invention consists of those which comprise:

(a) from 5% to 40%, preferably from 10% to 25% by weight of the aluminosilicate;

(b) from 0% to 10%, preferably from 0.3% to 5% by weight
20 of the organic liquid; and

(c) the balance being the water and one or more optional other ingredients.

One or more optional other ingredients may beneficially be incorporated in compositions according to any aspect of the present
25 invention, e.g. in amounts from 0.001% to 5%, such as 0.01% to 2% by weight of the composition for any or each class, and may for example be selected from any of the classes:

(i) one or more surfactants, preferably selected from anionic, nonionic, cationic, amphoteric and zwitterionic surfactants and
30 mixtures thereof, for example those which are known to be compatible with silicate and/or aluminate solutions, such as alkali caprybampho-

proprionates;

(ii) one or more phosphonates and/or phosphonic acids, such as tri-phenylphosphates and nitrilotric (methylene) triphosphoric acid;

5 (iii) one or more slow proton releasing inorganic salts such as dihydrogen aluminium phosphates;

(iv) one or more sequestrants such as EDTA or of the phosphonate type, e.g. those sold under the name Dequest; and

10 (v) one or more isocyanates such as methylene di-isocyanate.

The amount of water in such compositions is preferably from 60% to 95%, more preferably from 70% to 90% by weight of the total composition.

15 The aluminosilicate is typically amorphous. The mole ratio of Si:Al in the composition is typically from 3 to 30, preferably from 4 to 15 and more preferably from 5 to 10. In this context, the reference to mole ratio of Si:Al is based on the amount of silicon (in moles) in the silicate and aluminium (in moles) in the aluminate. The aluminosilicate is usually formed by the sol-gel route, preferably *in situ* from admixture
20 of precursor components at the point of use.

The compositions preferably also comprise a metal or metal oxide to aid preservation of the film forming properties of the composition, especially film integrity, upon storage. The metal or oxide will usually be in particulate form and be sparingly soluble in water.
25 Amphoteric or acidic oxides are typically employed for this purpose.

The metal oxide may, for example, be selected from zinc oxide, silicon oxide, aluminium oxide, boron oxide, tin oxide, gallium oxide, germanium oxide and mixtures of two or more of these oxides. Instead of introducing the metal in the form of an oxide, the oxide may
30 alternatively be formed *in situ* as a result of adding the metal *per se* to the composition. Without wishing to be bound by theory, it is believed

that the zinc or other oxide reacts with any residual silicate to reduce solubility of films formed by coating or otherwise applying the composition to foamed polymer.

5 Preferably also, the amount of the metal oxide or metal is up to 10%, preferably from 0.3% to 5% by weight (e.g. from 0.3% to 3% by weight) of the total composition.

The compositions preferably comprise from 0% to 10%, preferably from 0.3% to 5% (e.g. 0.3% to 4%) by weight of the organic liquid.

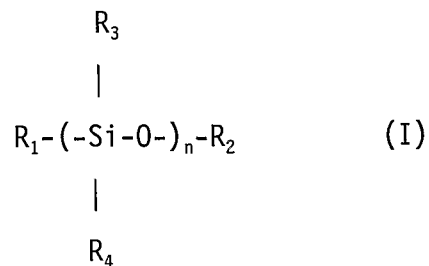
10 Preferably, it has a boiling point (at atmospheric pressure) of at least 110 °C, typically at least 130 °C and typically up to 500 °C.

The organic liquid is desirably one which is stable under alkaline conditions and also stable with respect to oxidation, heat and
15 light.

The organic liquid is typically one having a viscosity of less than 5000 mPa.s, preferably less than 2000 mPa.s (e.g. less than 1000 mPa.s), at a temperature of 25 °C.

20 The organic liquid may comprise one or more substantially water immiscible organic solvents selected from polyhydroxy alcohols, mineral oils, liquid paraffin oils, glycol ethers, silicone oils and mixtures thereof. Of these, silicone oils are especially preferred.

Suitable silicone oils for use in the compositions and precursor systems therefor, are organosiloxanes, typically having the
25 general formula (I):



wherein n is the number of repeating units in the polymer and can range from 2, e.g. from 10, up to 1,000,000, more preferably from 30, e.g. from 50, up to 500,000 and R₁ can be selected from hydrogen or methyl groups and R₂ can be selected from hydrogen or SiR₅ in which R₅ can be either hydrogen, hydroxyl or methyl and wherein R₃ and R₄ can be independently selected from C₁ to C₁₂ straight chain or branched, saturated or unsaturated alkyl, alkenyl or phenyl moieties or from units according to formula (I) above or from substituted alkyl or substituted phenyl moieties in which substituents can be halogens, amino groups, sulphate groups, sulphonate groups, carboxy groups, hydroxy groups or nitro groups.

The compositions (which may optionally be prepared from a precursor system at the point of use) may for example be applied to the foamed polymer by means of a spray gun (optionally air or gas pressurised), a roller system or a brush system. Alternatively the foamed polymer to be treated may be coated or impregnated by immersion in the coating composition while contained in a suitable vessel, for example in a fluid bed, an agitated bed or in a mixer like a ribbon blender.

The compositions which are to be used as fire retardants are especially suited to those which comprise an expanded or foamed polymer. Most preferably, that polymer is one which is substantially insoluble in the organic liquid, if present, at room temperature, i.e. the liquid component is selected with that requirement in mind.

Preferably, the moisture content of the resultant cured or

dried composition film, i.e. the coating, is no greater than 40%, more preferably no greater than 35% and still more preferably no greater than 20% by weight.

Preferred coatings have a long term solubility of no greater than 25%, typically no greater than 20%, preferably no greater than 15%, and more preferably no greater than 10%, as determined by the water resistance/solubility methodology defined hereinafter, after oven drying the film at 80 °C to a water content of about 17% and then soaking in water at a temperature of about 22 °C for 7 days.

The present invention will now be explained in more detail by way of the following non-limiting Examples.

Example 1: Preparation of Aluminosilicate Sol-Gel with a Molar Ratio of Si/Al of 8.5 (Comparative)

50 grams of sodium silicate solution (8.6% Na₂O, 29% SiO₂, balance water) was weighed directly into a plastic beaker. The silicate solution was vigorously stirred. To the vigorously stirred silicate solution, 40 grams of sodium aluminate solution (2.6% Na₂O, 3.6% Al₂O₃) was added dropwise over 3 to 4 minutes. After a further 10 – 20 seconds of mixing, stirring was stopped.

Approximately 25 grams of the resultant clear aluminosilicate sol formed was accurately weighed and poured onto a preweighed flat circular (~10 centimetre in diameter) plastic dish. The aluminosilicate sol was allowed to set for about 5 minutes to form a gel network. All of the foregoing steps were carried out under room temperature conditions (about 22 °C). The coated dish was placed in an oven at 80 °C for 24 hours and the plastic and the dried contents were then weighed. The dried aluminosilicate formed was a continuous and strong circular shaped sheet with about 1mm thickness and its solid content was 74% by weight (i.e. water content of 26% by weight).

Example 2: (Comparative)

The experiment of Example 1 was repeated but this time no aluminate solution was added and instead of the aluminate solution 37.5 grams of pure water was added.

5 Water Resistance/Solubility Methodology

In order to test water resistance/solubility, the following procedure is adopted:

10 The dried film is first broken into large (about 2 cm across) pieces. 2.0 g of the pieces are put in a sterlin jar and 28 g of water added. The pieces are fully submerged in the water and left to stand for 24 hours at ambient temperature (about 22 °C). The contents of the solution are analysed (using titration and gravimetric methods) and the solubility of the pieces after 24 hours soaking, is determined using the following formula:

15
$$\frac{\text{Dissolved contents in the solution} \times 100}{2.0}$$

20 When this procedure was applied to the film obtained in Example 1 and also to the film as obtained in Example 2, the following solubility results were obtained.

	<u>% Solubility</u>
Example 1	5
25 Example 2	100

30 These results clearly indicate that the formation of aluminosilicate films via the sol-gel process not only result in initially strong, solid films but also significantly enhances the water resistant property of the films produced.

The above results relate to a film which has been dried to a water content of 26% by weight. Elsewhere in this specification, the same methodology is employed except that the extent of drying and soaking may be varied as specified.

5 Example 3: Effect of Organic Liquid

The film formed in Example 1 was strong and clear. However, when such film was oven dried beyond 24 hours, it gradually started to form white patches and within 72 hours, it had turned to a weak and white flaky/powdery material.

10 To enhance the integrity of the aluminosilicate film beyond 24 hours drying, a small amount of organic liquid was added to the silicate solution of Example 1. Addition of 0.5 g of silicone oil with a viscosity of 50 mPa.s, for example, maintained the integrity of the aluminosilicate film even after 168 hours of oven drying at 80 °C. A
15 number of organic liquids having various boiling points (BP) were tested and their impact on the integrity of aluminosilicate film after prolonged drying (168 hours of oven drying at 80 °C) are given below:

	<u>Organic Liquid tested</u>	<u>BP(°C)</u>	<u>Film Integrity</u>
20	Hexamethyl Silazane	110	Powdery, white
	Hexamethyl Disiloxane (0.65 mPa.s))	100	Powdery, white
	Silicone Oil (10 mPa.s)	>150	Clear, non-powdery
	Silicone Oil (20 mPa.s)	>150	Clear, non-powdery
	Silicone Oil (50 mPa.s)	>150	Clear, non-powdery
25	Silicone Oil (200 mPa.s)	>150	Clear, non-powdery
	Silicone Oil (1000 mPa.s)	>150	Clear, non-powdery
	Liquid Paraffin Oil	~300	Clear, non-powdery

30 Example 4: (Effect of Film Moisture Content on Water Resistance)

The dried film made according to Example 1 had a moisture

content of 26%. When this film was soaked for 24 hours, it remained fairly intact. However, when the soaking in water was extended to 3 and then to 7 days, the solubility of the film increased proportionally. Reducing the moisture content of the film by for example prolonging drying time, would have minimised its water solubility. However, this is not an option for a film produced according to Example 1 as prolonged drying to minimise its moisture content, will result in weak and powdery film. However, the film made according to Example 3 (i.e. containing silicone oil) has no such problem, and thus the film of Example 3 was dried to longer times to generate films with different moisture contents. The effect of film moisture content on the solubility of such film was conducted and the results are given below:

Solubility Results

	<u>Days Soaked in Water</u>		
	<u>1</u>	<u>3</u>	<u>7</u>
<u>% Moisture Content of Film</u>			
26	5%	20%	47%
22	4%	15%	30%
17	3%	4%	5%

The above table clearly indicate that an aluminosilicate film containing a water immiscible liquid such as silicone oil and having a moisture content of about 17% is significantly more resistant to water.

Example 5: (Long Term Water Resistance)

The aluminosilicate film (with moisture content of 17%) made according to Example 4 and soaked for 7 days has good water resistance. However, when the same film is soaked for more than 7 days, for example 10 and 25 days, its water resistance decreases with increased soaking time.

To further improve the long-term water resistance of the

aluminosilicate film, Example 4 was repeated but 1 gram of zinc oxide was added to and thereby suspended in the silicate and silicone oil mixture. The solubility of films made according to Examples 4 and 5 (with moisture contents of 17%) were assessed using the methodology defined hereinbefore using soaking times of 7, 10 and 25 days. The following results were obtained:

Solubility after Soaking for 7, 10 and 25 Days

	<u>7 days</u>	<u>10 days</u>	<u>25 days</u>
<u>Sample</u>			
Example 4 (without Zinc Oxide)	3%	10%	30%
Example 5 (with Zinc Oxide)	1%	1.3%	4%

As can be seen from the above results, addition of a small amount of zinc oxide enhances the long-term water resistance of films produced using aqueous aluminosilicate compositions obtained by the sol-gel route.

Example 6: (Production of Aluminosilicate Sol-Gel Film (Si/Al Ratio of 8.5) Using an In-Line Mixer)

To stirred 1335 grams of sodium silicate solution (17.1% Na₂O, 23.9% SiO₂, balance water), 11 grams of silicone oil (viscosity 20 mPa.s at 25 °C) was added. The silicone oil silicate mixture and sodium aluminate solution (4.6% Na₂O, 5.6% Al₂O₃) were simultaneously pumped to a high shear in-line mixer (with inlet ports adapted to suit the viscosity of the resultant sol) at the rate of 253 ml/minute and 107 ml/minute respectively. A clear aluminosilicate sol was formed and a sample of this sol was treated and characterised in the same way as in Example 1.

Example 7

The same as Example 6 but with 22 grams of zinc oxide added to the silicate/silicone mixture.

The results of solubility tests for samples of Examples 6 and 7 dried to moisture content of 17% and soaked in water for 7, 10 and 14 days were as follows:

5 Solubility after Soaking for 7, 10 and 14 Days

	<u>7 days</u>	<u>10 days</u>	<u>14 days</u>
<u>Sample</u>			
Example 6 (without Zinc Oxide)	2.7%	9.5%	13%
Example 7 (with Zinc Oxide)	1%	1.2%	2.2%

10

Example 8: Coating of beads in a fluidized bed followed by shape moulding

Prime regular EPS beads with a size of 1.0-1.6 mm were preexpanded using a batch preexpander to a density of 20 kg/m³, with a preexpansion pressure of 0.25 bar. After pre-expansion a bead size of the EPS of 3-4 mm is obtained and this is used for coating with the mixture according to Example 7. These beads are placed in a fluidized bed, where the airflow can be set to lift the beads. The airflow is low to begin with and increases proportionally as the coating is applied, so as to continue to levitate the beads of which the density increases when more mixture is sprayed onto the beads.

Beads coated with the mixture are stored in an intermediate silo and thereafter transferred to a closed mould of 1 x 1 x 0.1 m. This mould has core vents at regular distances through which the steam can be applied to the mixture of loose beads coated with the mixture.

The mixture becomes slightly viscous by heating with the steam, provided that the DS (dry solid) content lies in between 75 to 85% and the expansion of the EPS beads ensures that the open spaces between the individual beads are filled as a result of the further expansion.

On making a cross section a honeycomblike structure is obtained where the mixture has deformed and forms a continuous network.

The EPS beads are merely a carrier for the mixture.

Sheets were produced with densities of 80 and 150 kg/m³. The sheets were tested in water of 20 °C during 2 weeks and it maintained their structural integrity. The weight loss, measured after drying of the sheet, was < 5%. To the surprise of the inventors when tested according to DIN 4102 B2 these sample passed this test, which is normally only possible with flame retardant EPS.

Example 9: Coating of 50% recycled EPS, 50% pre-expanded EPS in a fluidized bed followed by shape moulding

In another embodiment of the invention the mixture according to Example 7 was sprayed onto a mixture of pre-expanded EPS and packaging waste ground to a size of 4-5 mm Recycled-EPS or REPS in a ratio of 50/50 EPS/REPS. This mixture was placed in a fluidized bed, where the airflow can be set to lift the beads. The airflow is low to begin with and increases proportionally as the coating is applied, so as to continue to levitate the beads of which the density increases when more mixture is sprayed onto the 50/50 mixture.

Beads coated with the mixture are stored in an intermediate silo and thereafter transferred to a closed mould of 1 x 1 x 0.1 m. This mould has core vents at regular distances through which the steam can be applied to the 50/50 ERPS/REPS coated with the mixture.

The properties of the product thus obtained are equal to the results of Example 8.

Example 10: Coating of Arcel EPS in a fluidized bed followed by shape moulding

In another embodiment of the invention the mixture according to Example 7 was sprayed onto Arcel beads (trademark of Nova Chemical, a polymeric mixture of PS and PE).

Arcel beads fluidized bed coated with the mixture are stored in an intermediate silo and thereafter transferred to a closed mould of 1 x 1 x 0.1 m.

The properties of the product thus obtained are equal to the results of Example 8.

Example 11: Coating of EPP foam beads in a fluidized bed followed by shape moulding

5 In another embodiment of the invention the mixture according to Example 7 was sprayed onto EPP beads. EPP beads are polymeric foam polypropylene are e.g. traded under the name Neopolene by BASF. EPP beads were used in a density of 40 g/m³ and a size of 5-7 mm. This mixture was placed in a fluidized bed, where the airflow can be set
10 to lift the beads.

EPP beads coated with the mixture according to Example 7 are stored in an intermediate silo and thereafter transferred to a closed mould of 1 x 1 x 0.1 m.

15 The properties of the product thus obtained are equal to the results of Example 8.

CLAIMS

1. A method of manufacturing a fire retardant composite, the method comprising the following steps:

- 5 i) providing beads of foamed polymer,
 ii) applying a coating on the beads of step i) and
 iii) shaping the thus coated beads into said composite.

2. A method according to claim 1, in which step iii) is carried out in a press.

10 3. A method according to claim 1, in which step iii) is carried out as a casting method.

4. A method according to claim 1, in which step ii) is carried out in a fluid bed, wherein the coating is sprayed on the beads and an air flow is blown through the bed of beads.

15 5. A method according to claim 1, in which step ii) is carried out in an agitated bed, wherein the coating is sprayed onto the beads.

6. A method according to claim 1, in which step ii) is carried out in a mixer, for example a ribbon blender, wherein the coating is sprayed on the beads.

20 7. A method according to claim 2, in which step iii) comprises further steps iv), v) and vi), in which step iv) transferring the coated beads to a press, v) applying steam to the coated beads present in said press, and vi) releasing the composite from the press.

8. A method as claimed in any one of the preceeding claims in which the foamed polymer is selected from PUR, PET, EPP, EPE, expanded polyvinyl arylenees or a combination thereof.

25 9. A method as claimed in any one of the preceeding claims in which the coating is an aqueous gel-forming composition, comprising:

30 (a) from 5% to 40%, preferably from 10% to 25% by weight of an aluminosilicate;

 (b) 0 to 10%, preferably from 0.3% to 5% by weight of a

film-integrity enhancing organic liquid; and

the balance being the water and one or more optional other ingredients.

10. A method as claimed in claim 9, in which the organic liquid has a boiling point of at least 110 °C, preferably at least 130 °C.

11. A method as claimed in any one of the preceding claims 9-10, in which the organic liquid is substantially water immiscible.

12. A method as claimed in any one of the preceding claims 9-11, in which the organic liquid is one which is stable under alkaline conditions.

13. A method as claimed in any one of the preceding claims 9-12, in which the organic liquid is one which has a viscosity of less than 5000 mPa.s, preferably less than 2000 mPa.s, at a temperature of 25 °C.

14. A method as claimed in any one of the preceding claims 9-13, in which the organic liquid is a liquid selected from polyhydroxy alcohols, mineral oils, liquid paraffin oils, glycol ethers, silicone oils and mixtures thereof.

15. A method according to any one of the preceding claims 9-14, further comprising at least one metal or metal oxide for aiding preservation of film integrity when the composition is applied as a coating to a surface.

16. A method as claimed in claim 15 in which the metal oxide is an amphoteric oxide.

17. A method as claimed in claim 15 in which the metal oxide is an acidic oxide.

18. A method as claimed in claim 15 in which the metal oxide is selected from zinc oxide, silicon oxide, aluminium oxide, boron oxide, tin oxide, gallium oxide, germanium oxide and mixtures of two or more of these oxides.

19. A method as claimed in any one of claims 15-18 in which the

metal or metal oxide thereof comprises up to 10%, preferably up to 5% by weight of the total composition.

20. A method as claimed in any one of claims 15 to 19 in which the metal or metal oxide thereof is in particulate form.

5 21. A method as claimed in any one of the preceding claims 9-20, in which the aluminosilicate has a Si:Al mole ratio of from 3 to 30, typically up to 15, preferably up to 10.

10 22. A method as claimed in any of the preceeding claims 9-21, in which the coating is a solution of a metal aluminate and a metal silicate and, if appropriate, one organic liquid selected from the group comprising polyhydroxy alcohols, mineral oils, liquid paraffin oils, glycol ethers, silicone oils and mixtures thereof.

23. A method as claimed in any one of the preceeding claims 9-22, in which the coating is a precursor system comprising:

- 15 (i) water and a metal aluminate;
(ii) water and a metal silicate; and, if appropriate,
(iii) said organic liquid.

24. A method as claimed in any of the preceeding claims 9-23, in which the foamed polymer has a density of 5-500 kg/m³.

20 25. A method as claimed in any of the preceeding claims 9-23, in which the foamed polymer including the coating has a density of 10-1000 kg/m³, on a dried coating basis.

25 26. A composite of a foamed polymer having a coating with fire retardant properties, characterised in that the coating is produced using an aqueous gel-forming composition, comprising an aluminosilicate composition, and one or more optional other ingredients.

27. A composite according to claim 26, in which the aqueous gel forming composition further comprises a film-integrity enhancing organic liquid.

30 28. A composite according to claims 26-27, in which the aluminosilicate composition is from 45% to 90% by weight, on basis of the

dried coating.

29. A composite according to claim 28, in which the aluminosilicate composition is from 50% to 85%, by weight, on basis of the dried coating.

5 30. A composite as claimed in any one of the preceeding claims 26-29 in which the moisture content of the dried coating is no greater than 40%, preferably no greater than 35% and more preferably no greater than 20% by weight.

10 31. A composite as claimed in claim 30 in which the dried coating has a moisture content of 16%, by weight, or less.

32. A composite as claimed in any one of the preceeding claims 26-31 in which the coating further comprises at least one metal or metal oxide in an amount of up to 16%, preferably up to 8% by weight of the dried coating.

15 33. A composite as claimed in any one of the preceeding claims 27-32 in which the organic liquid comprises up to 16% by weight of the dried coating.

20 34. A composite as claimed in any one of the preceeding claims 26-34 in which the aluminosilicate has a Si:Al mole ratio of from 3 to 30, typically up to 15, preferably up to 10.

35. The use of a composite according to any one of the claims 26-34 as a construction material.

36. The use according to claim 35 in buildings.

25 37. The use of a composite according to any one of the claims 26-34 as an insulant.

38. The use according to claim 37 in buildings.

39. The use according to claim 35-36, in which the construction material is chosen from the group panel, door, sheeting, ceiling and tile.

30 40. The use of a composite according to any one of the claims 26-34 as a construction material for packaging.

INTERNATIONAL SEARCH REPORT

ational application No

/NL2005/000546

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/224 C08J9/232 C09K21/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08J C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 369 134 A (GRAB ET AL) 29 November 1994 (1994-11-29)	1-8, 12-15, 19,20,24 9
Y	example 1 column 1, line 43 - column 2, line 68 claims	
Y	US 6 197 415 B1 (HOLMAN MARK E) 6 March 2001 (2001-03-06) claims	9
A	US 5 462 699 A (MONTGOMERY ET AL) 31 October 1995 (1995-10-31) cited in the application claims	9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Oudot, R

INTERNATIONAL SEARCH REPORT

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/NL2005/000546

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